

REPORT DOCUMENTATION PAGEForm Approved
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE March 15, 2002	3. REPORT TYPE AND DATES COVERED Final Report - March 1997 - December 2001
4. TITLE AND SUBTITLE Studies on the Microwave Optics of Ionic Molecular Solids		5. FUNDING NUMBERS DAAG55-97-1-0106	
6. AUTHOR(S) Dr. John R. Hardy			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Nebraska-Lincoln Lincoln, NE 68588-0111		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>35869.15-PH</i>	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Work carried out under this grant is summarized. In particular, the prediction of a novel ferroelectric material NaCaF_3 is described and its predicted properties summarized. First principles calculations on a wide range of ionic molecular solids are summarized. These range from studies on halide perovskites to work on alkaline earth silicates. In most cases very reasonable accord with experiment is achieved. One notable exception is the class of alkali cyanides which clearly require more sophisticated treatment. The basic theoretical approach is a combination of a Gordon-Kim modified electron gas theory with the quantum chemistry GAUSSIAN code to handle covalently bonded molecular ions. As indicated, this parameter free treatment reproduces experimental phase diagrams with good accuracy.			
14. SUBJECT TERMS ferroelectrics, microwaves, quantum chemistry		15. NUMBER OF PAGES 17	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
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298-102

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REPORT TITLE: Studies on the Microwave Optics of Ionic Molecular Solids-Final Report

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Sincerely,

Dr. John R. Hardy

**Studies on the Microwave Optics of
Ionic Molecular Solids**

Final Report

John R. Hardy

March 15, 2002

U.S. Army Research Office

DAAG55-97-1-0106

**Department of Physics and Center for Electro-Optics
University of Nebraska-Lincoln
Lincoln, NE 68588-0111**

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INTRODUCTION

The current program is a continuation of our previous studies on the "computer engineering" of ionic molecular solids. The basic aim of the program is the predictions of physical properties by First Principles calculations entirely free from disposable parameters.

Our principal theoretical tool is the Gordon-Kim form of the modified electron gas approximation, supplemented by quantum chemistry for the treatment of covalently bonded molecular groups, e.g., SO_4^{2-} . Most recently this has been supplemented by the self-consistent atomic deformation model (SCAD) and full augmented plane wave band structure calculations. In addition, studies have been made on the phase diagrams of binary mixtures of different fluorides. One material we have particularly emphasized is sodium calcium trifluoride. While this has only been synthesized in the computer, its predicted properties are so interesting that actual physical synthesis could produce a material with extremely useful properties. Specifically, we find it to assume the lithium niobate structure with a ferroelectric polarization at ambient temperature comparable to barium titanate. This suggests that it is a candidate for ferroelectric applications which could be superior to conventional oxide-based systems. In particular, it is transparent well into the ultra violet (UV) and could, for example, provide a non-linear material for UV optics, as distinct from oxides which are opaque in this spectral range.

Since the abstracts of our relevant publications contain a full summary of each investigation, we shall use these interspersed with appropriate introductory material.

Studies on Mixed Fluorides

These are described in the following two abstracts. In one case, KCaF_3 is mixed with RbCaF_3 , in the other the components are NaMgF_3 and KMgF_3 .

As can be seen agreement between theory (Gordon-Kim) and experiment is good, in particular an observed eutectic point in the KMgF_3 , NaMgF_3 , phase diagram is reproduced by theory.

Structural Phase Transitions in Ionic Molecular Solids

This is a general review paper which discusses at length the basic principles which govern the origins of incommensurate phases in these systems. It brings together a wide range of our earlier results in order to exemplify these principles.

Structural Phase Transitions in Systems with Linear Molecular Ions

These papers discuss the order-disorder transitions in alkali azides, thiocyanates, cyanides and thallium azide. All of these compounds are either distorted NaCl or CsCl structures. The transitions involve hindered rotations of the linear ions producing a variety of high temperature phases, some of which while predicted theoretically, are pre-empted by melting in the real systems.



Pergamon

Materials Research Bulletin, Vol. 31, No. 9, pp. 1093-1099, 1996
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0025-5408/96 \$15.00 +.00

PII S0025-5408(96)00099-2

**PHASE TRANSITIONS IN
MIXED ALKALI CALCIUM TRIFLUORIDE SOLID SOLUTIONS**

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(Refereed)

(Received April 22, 1996; Accepted May 20, 1996)

ABSTRACT

Both KCaF_3 and RbCaF_3 are known to undergo ferroelastic phase transitions, the former at temperatures near 550 K and the latter at 195 and 40 K. The two compounds comprise ends of the completely miscible solid solution $\text{K}_{1-x}\text{Rb}_x\text{CaF}_3$. Simulations of molecular dynamics have been performed for this solid solution, where Rb^+ ions were substituted for K^+ ions in KCaF_3 in varying concentrations of randomly distributed defects representing constitutional crossover to RbCaF_3 . First-principles calculations were used to obtain the potentials between ion pairs in these samples; the pair potentials were used to calculate the temperature dependence of the interaxis angles which were used as markers for the polymorphic phase transition. The calculated transition temperature thus obtained decreases in a nearly linear fashion as a function of Rb^+ ion concentration. Experimental transition temperatures obtained from differential scanning calorimetry of actual samples agree well with the calculated temperatures for those compositions with transitions above room temperature.

KEYWORDS: A. fluorides, C. differential scanning calorimetry (DSC), D. phase transitions



Pergamon

Materials Research Bulletin 35 (2000) 341–349

Materials
Research
Bulletin

Polymorphic phase transitions in mixed alkali magnesium fluoride solid solutions

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(Refereed)

Received 17 May 1999; accepted 24 May 1999

Abstract

Phase transitions in the miscible solid solution $\text{Na}_{1-x}\text{K}_x\text{MgF}_3$ were examined over a wide range of compositions by computer molecular dynamics, X-ray diffraction, and thermal analysis in order to characterize the polymorphic phase transitions as a function of alkali-metal content. The pure NaMgF_3 composition has a single orthorhombic-to-cubic transition at 1038 K, but computer modeled compositions with K^+ partially substituted for Na^+ ions have at least two polymorphic transitions. The models also indicate that the transition temperatures decrease with increasing potassium content. Results from thermal analyses and from literature give similar results. Computer simulations, experimental data, and literature values all show a room-temperature transition for the composition around $\text{Na}_{0.65}\text{K}_{0.35}\text{MgF}_3$. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Fluorides; C. Differential scanning calorimetry (DSC); C. X-ray diffraction; D. Lattice dynamics; D. Phase transitions

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Structural Phase Transitions in Ionic Molecular Solids Abstract

Phase Transitions, Vol. 67, pp. 521-537
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STRUCTURAL PHASE TRANSITIONS IN IONIC MOLECULAR SOLIDS*

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An overview is presented of our studies on the nature of structural instabilities in relatively complex ionic solids. These are based on parameter-free interionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

We describe the manner in which there emerge from these studies quite general concepts of "size" and "shape" as structural determinants. In particular, we discuss how these, and the approximate symmetries that they can produce, can provide a relatively simple structure-based explanation of the origins of incommensurate phases in these systems. However, we also emphasize that the existence of such symmetries does *not guarantee* an incommensurate phase. This can only be realized if long-range correlations are sufficiently strong to overcome random local disordering. Thus, either the molecular units are partially linked and/or there exist long-range Coulomb interactions between individual units.

Keywords: Lattice dynamics; Ionic molecular solids; Incommensurate structures

Perhaps the most interesting system is KSCN. Experimentally, this appears to assume a tetragonal structure just prior to melting. However, microscopically, it is found to consist of dynamically moving domains of the low-temperature orthorhombic phase. Theoretically, our molecular dynamics supercell is far too small to reveal this behavior. However, what we do observe is the onset of CN^- flipping out of the basal plane. We argue that this is the origin of the moving domain walls producing the dynamically twinned structure observed experimentally.

One of other significant finding is that our combined quantum chemistry Gordon-Kim approach produces activation barriers for CN^- rotations that are far too high, indicating that a more sophisticated approach (e.g., SCAD) is necessary for these strongly polar ions.

More Sophisticated First Principles Studies

The first two investigations under this heading are applications of the self-consistent atomic deformation model (SCAD). In this model, localized atomic states centered on the respective ions are used. Each is then calculated self-consistently in the crystal field of the other ions. Thus, as the lattice is deformed, the ions deform in a self-consistent manner; the deformation at each site being consistent with the field at that site due to the other (deformed) ions. Hence, the overall charge distribution and total energy change are self-consistent.

In the first study, the method is applied to the alkali halide sequence with very reasonable results: in particular, polar motions produce Born effective charges in good accord with experiment as distinct from the simple Gordon-Kim result of unity in all cases.

In the second study, the method is applied to NaCaF_3 to examine the effect of this modification on the ferroelectric behavior of this system. Once again, the system is found to be ferroelectric with a well depth comparable to the Gordon-Kim value. Also, the compound remains metastable with respect to the constituents NaF and CaF_2 .

Finally, we present a first principles study of the optical (linear and non-linear) properties of KNbO_3 .

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach

This approach is that employed in our previous work on ionic molecular systems. The molecular ion charge density is calculated using the GAUSSIAN Quantum Chemistry package and it is then decomposed into individual atomic components which are employed in a Gordon-Kim derivation of all potentials external to the group. The internal motion is treated within the harmonic approximation using force constants generated by GAUSSIAN. For the monatomic cations, charge densities calculated from the tabulated wave functions are employed in the respective Gordon-Kim calculations.

Structural Phase Transitions in Systems with Linear Molecular Ions Abstract

PHYSICAL REVIEW B

VOLUME 60, NUMBER 22

1 DECEMBER 1999-II

Molecular-dynamics study of phase transitions in alkali azides

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(Received 18 June 1999)

An account is presented of our studies of the order-disorder phase transitions in KN_3 , RbN_3 , and CsN_3 . These are based on parameter-free interionic potentials based on the Gordon-Kim modified electron-gas formalism extended to molecular ions. We performed static structural relaxations and supercell molecular dynamics and predicted with reasonable accuracy the temperatures for the onset of the transitions. In particular, we address the question of how the N_3^- ions reorient to yield the transitions. We found the existence of NaCl-type high-temperature phases in disordered KN_3 and RbN_3 and argue that this restructuring is preempted by melting in these two systems. [S0163-1829(99)10541-1]

PHYSICAL REVIEW B

VOLUME 62, NUMBER 5

1 AUGUST 2000-I

Molecular-dynamics study of phase transitions in alkali thiocyanates

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(Received 22 November 1999)

An account is presented of our studies of the order-disorder phase transitions in KSCN , RbSCN , and CsSCN . These are based on parameter-free interionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions. We performed static structural relaxations and supercell molecular dynamics and predicted with reasonable accuracy the temperatures for the onset of the transitions. In particular, we address the question of how the SCN^- ions disorder to yield subsequent structural transformations. We found high-temperature phases of average $Fm\bar{3}m$ symmetry for both KSCN and RbSCN . We argue that in reality the full appearance of these phases is preempted by melting. However, they are candidates for the twin boundaries which are observed in the high-temperature "average" tetragonal phases. The high-temperature phase of CsSCN was found to be of average $Fm\bar{3}m$ symmetry.

Computer Molecular Dynamics and Phase Transitions in Alkali Azides and Thiocyanates

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ABSTRACT

An account is presented of our studies of the order-disorder phase transitions in KN_3 , RbN_3 , CsN_3 , KSCN , RbSCN and CsSCN . These are based on parameter-free inter-ionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

With these potentials we performed static structural relaxations and supercell molecular dynamics and predict with reasonable accuracy the temperatures for the onset of the transitions. In particular we address the question of how the N_3^- and SCN^- ions reorient to yield the transitions.

It was found that in case of azides we observed hindered rotations of the anions about all three crystallographic axes, in all three systems. However, in the thiocyanates only CsSCN yielded hindered rotations about all three axes. In KSCN and RbSCN the order-disorder transition appears rather to involve large amplitude librations of the SCN^- ions, primarily about the c axis.

Keywords: Azides; Thiocyanates; Ionic molecular solids; Phase transitions



Pergamon

Materials Research Bulletin 36 (2001) 2035–2041

Materials
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High-temperature phase transition in TiN_3

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(Refereed)

Received 9 January 2001; accepted 9 May 2001

Abstract

The phase transition in TiN_3 is simulated based on the potentials calculated from the Gordon-Kim modified electron gas model extended to ion molecular crystals. It is found that TiN_3 transforms into a cubic CsCl structure at high temperature due to the rotations of the N_3 ions. Above the phase transition the orientations of the N_3^- ions are random with four preferred orientations with respect to the cubic axes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: D. phase transitions

Structural Transitions in NaCN and KCN

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Abstract. An account is presented of our studies of the order-disorder phase transitions in NaCN and KCN. These are based on parameter-free inter-ionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

We performed static structural relaxations and supercell molecular dynamics and reproduced two transitions known in each of these systems.

We also calculated upper bounds to the barrier of rotation of a cyanide ion in a ground state of NaCN and KCN and discuss possible shortcomings of our model.

More Sophisticated First Principles Studies Abstract

PHYSICAL REVIEW B

VOLUME 61, NUMBER 17

1 MAY 2000-1

Calculation of electronic, structural, and vibrational properties in alkali halides using a density-functional method with localized densities

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(Received 7 December 1999)

A recently developed density-functional method based on localized densities is applied to calculate electronic, structural, and vibrational properties of 20 alkali halides with elements lithium through cesium and fluorine through iodine. Properties calculated include dissociation energy, lattice parameter, dielectric constant, elastic moduli, and phonon frequencies for the high-symmetry points of the Brillouin zone. Results are discussed and compared with experiment and other calculations.

More Sophisticated First Principles Studies Abstract

Predicted Properties of NaCaF_3

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Abstract. More than a decade ago computer simulations based on Gordon-Kim potentials suggested that NaCaF_3 would be a ferroelectric compound if it could be formed experimentally. Recent attempts to form thin films of NaCaF_3 using pulsed-laser deposition have prompted us to carry out further theoretical studies of this material. Here we apply the self-consistent atomic deformation method to calculate electronic, structural and vibrational properties of NaCaF_3 and the constituent compounds NaF and CaF_2 .

First-principles study on the optical properties of KNbO_3

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Received 19 June 2001, in final form 17 July 2001

Published 16 August 2001

Online at stacks.iop.org/JPhysCM/13/S189

Abstract

We report our studies on the electronic structure and linear and nonlinear optical (NLO) properties of KNbO_3 using a first-principles method in the local density approximation (LDA). The calculated results for the refractive indices and second-harmonic-generation (SHG) coefficients agree well with experimental results. From decomposing the nonlinear susceptibility, we find that the primary contribution to the NLO behaviour comes from the hybridization of the O 2p and Nb 4d electron states. In addition, there are two different roles played by the O atoms because of their different distances from the Nb atom: thus we propose a possible way to enhance the SHG coefficients.

The following compounds have been studied: alkali nitrites; isomorphous NaNO_3 and CaCO_3 ; RbNO_3 and CsNO_3 ; AgNO_3 ; alkali perchlorates; and alkaline earth silicates.

As before, this work is detailed in the following abstracts of the respective studies.

The nitrites are of particular interest insofar as the NO_2^- ion has a permanent dipole and thus, in the high temperature phases where these ions are in quasi-free rotation, they can couple to an applied microwave field and provide loss and optical dispersion. These compounds thus have potential applications for microwave optics. Of the other compounds, the silicates, in particular, are of geophysical interest - specifically their phase diagrams are the subject of controversy and our results may serve to settle this dispute.

PERSONNEL

Principal Investigator: Dr. John R. Hardy

Graduate Student/Postdoctoral Research Associate: Martin Ossowski

Visiting Scholar: Jianjun Liu

Further Studies on Ionic Molecular Solids within the Gordon-Kim Lu-Hardy Approach Abstract

PHYSICAL REVIEW B, VOLUME 63, 144105

Order-disorder phase transitions in KNO_2 , CsNO_2 , and TlNO_2 crystals: A molecular dynamics study

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(Received 5 January 2000; revised manuscript received 14 November 2000; published 16 March 2001)

The order-disorder phase transitions of KNO_2 , CsNO_2 , and TlNO_2 have been studied using parameter-free molecular dynamics simulation. It is found that the phase transitions in nitrites investigated are driven by the rotations of the NO_2^- ions about different axes together with displacements of cations and anions. We successfully reproduce the high-temperature phases of these nitrites, i.e., the NaCl-like structure for KNO_2 and CsCl-like structure for Cs(Tl)NO_2 . Based on the investigation of the radial distribution function of the cations and anions, we explain why KNO_2 and Cs(Tl)NO_2 form quite different low-temperature phases.

DOI: 10.1103/PhysRevB.63.144105

PACS number(s): 64.60.Cn, 61.43.Bn, 64.70.Pf

Phys Chem Minerals (2001) 28: 586–590

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ORIGINAL PAPER

Jianjun Liu · C.-G. Duan · M. M. Ossowski
W. N. Mei · R. W. Smith · J. R. Hardy

Simulation of structural phase transition in NaNO_3 and CaCO_3

Received: 30 January 2001 / Accepted: 11 May 2001

Abstract The order-disorder phase transitions in NaNO_3 and CaCO_3 are simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon-Kim modified electron gas formalism extended to molecular ions. We successfully reproduced the transition temperature T_c and the abnormally large c axis thermal expansion observed in experiment. The phase transitions in NaNO_3 and CaCO_3 were found to be initiated by $\pm 60^\circ$ and $\pm 180^\circ$ reorientation of the NO_3^- and CO_3^{2-} ions about the c axis. The orientations of NO_3^- and CO_3^{2-} ions are continuous with six preferred calcite-type orientations above the phase-transition temperature.

Key words Molecular dynamics simulation ·
Gordon-Kim potentials · Phase transition

**Further Studies on Ionic Molecular Solids within the Gordon-Kim
Lu-Hardy Approach Abstract**

**Simulation of Structural Transformation
in Aragonite CaCO_3**

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Abstract. The structural transformation in aragonite CaCO_3 is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon-Kim modified electron gas formalism. We found two phase transitions in aragonite at high temperature.

CP535, *Fundamental Physics of Ferroelectrics 2000*, Aspen Center for Physics Winter Workshop, edited by R. E. Cohen
© 2001 American Institute of Physics 1-650-950-6525/01/0

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Journal of Solid State Chemistry 160, 222-229 (2001)

doi:10.1006/jssc.2001.9226, available online at <http://www.idealibrary.com> on IDEAL[®]

**Molecular Dynamics Simulation of Structural Phase Transitions
in RbNO_3 and CsNO_3**

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Received January 12, 2001; in revised form April 18, 2001; accepted April 30, 2001

Structural phase transitions in RbNO_3 and CsNO_3 are studied by molecular dynamics. The simulations are based on the parameter-free potentials calculated from the Gordon-Kim modified electron gas formalism, extended to ionic molecular crystals. The microscopic mechanism of the structural phase transitions in RbNO_3 and CsNO_3 is revealed. It is found that the phase IV-III transition in RbNO_3 and the phase II-I transition in CsNO_3 are initiated by the in-plane and out-of-plane rotations of the NO_3 ions, and the phase III-II-I transitions in RbNO_3 are due to dilation along a trigonal axis of phase III, giving phase II a rhombohedral structure. © 2001 Academic Press

Key Words: molecular dynamics; Gordon-Kim potential; nitrate; phase transition; order-disorder.

**Further Studies on Ionic Molecular Solids within the Gordon-Kim
Lu-Hardy Approach Abstract**



Journal of Physics and Chemistry of Solids 63 (2002) 409–414

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

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Molecular dynamics simulation of phase transition in AgNO_3

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Received 12 January 2001; accepted 30 April 2001

Abstract

Structural phase transition in AgNO_3 at high temperature is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon–Kim modified electron-gas formalism extended to molecular ionic crystals. AgNO_3 transforms into rhombohedral structure at high temperature and the phase transition is associated with the rotations of the NO_3 ions and displacements of the NO_3 and Ag ions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: A. Inorganic compounds; C. Ab initio calculations; D. Phase transitions

Journal of Solid State Chemistry 163, 294–299 (2002)

doi:10.1006/jssc.2001.9411, available online at <http://www.idealibrary.com> on IDEAL[®]

Order–Disorder Structural Phase Transitions in Alkali Perchlorates

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Received June 15, 2001; in revised form September 20, 2001; accepted September 27, 2001

Order–disorder structural phase transitions in alkali perchlorates MClO_4 ($M = \text{Na, K, Rb, Cs}$) are investigated using molecular dynamics simulation. The potentials in the simulations are based on the Gordon–Kim modified electron gas formalism extended to molecular ions. The simulations yield first-order phase transitions in perchlorates from low temperature orthorhombic structures to high temperature cubic NaCl structures. The perchlorate ions are found to be orientational disordered in the high temperature phases. © 2002 Elsevier Science

Key Words: alkali perchlorate; molecular-dynamics simulation; phase transition; Gordon–Kim potential; order–disorder.

**Further Studies on Ionic Molecular Solids within the Gordon-Kim
Lu-Hardy Approach Abstract**

JOURNAL OF CHEMICAL PHYSICS

VOLUME 116, NUMBER 9

1 MARCH 2002

Polymorphous transformations in alkaline-earth silicates

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(Received 20 September 2001; accepted 3 December 2001)

Structural phase transitions in Ca_2SiO_4 and Sr_2SiO_4 are investigated by molecular dynamics simulations. The simulations are based on the potentials calculated from the Gordon-Kim modified electron gas formalism extended to molecular ions. We successfully reproduced the transition $\gamma - \alpha'_H - \alpha$ and $\beta - \alpha'_L - \alpha'_H - \alpha$ in Ca_2SiO_4 , and the transition $\beta - \alpha'$ in Sr_2SiO_4 . We find that the α'_L phase of Ca_2SiO_4 is an $a \times 3b \times c$ superstructure of the α'_H phase, while the α'_H phase has a $\beta\text{-K}_2\text{SO}_4$ structure, and the α phase of Ca_2SiO_4 has a disordered structure with space group $P6_3/mmc$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1446043]